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14. ABSTRACT Summary: Sodium metal can be made by electrolysis of molten sodium hydroxide in sodium beta-alumina membrane electrolysis cells. However, there are some uncertainties about the lifetime of the sodium beta-alumina membranes in contact with molten sodium hydroxide. The main objective of this project is to address these uncertainties and to study if the properties of the membrane degrade upon long term contact with molten sodium hydroxide. Electrolysis cells were designed, but it proved impossible to test them because the potentiostat that was to be used was designed for low current density. It therefore turned out to be impossible to do electrolysis tests with this experimental set-up. Instead, samples of sodium beta-alumina disk were aged in molten sodium hydroxide for up to 149 day. Mass loss was only 0,15 % in the first 108 days, but in the next 41 days mass loss accelerated considerably, or up to 0,33% in 41 days. No change in the phase composition of the material was observed in the 149 days. Investigation of aged samples with SEM (Scanning electron microscopy) revealed that the molten sodium hydroxide preferably dissolved material at grain boundaries, which most likely resulted in freeing of grains (1 to 3 micron diameter) from the bulk of the material. Conclusions 1. Sodium beta-alumina membranes were aged in molten NaOH at 340 C for 38, 108 and 149 days respectively. Samples were weighed and investigated in an SEM after each period. Rate of mass loss increases significantly in the period after 108 days, or from $1 \text{ to } 2 \times 10^{-3} \text{ %/day}$ to $8 \times 10^{-3} \text{ %/day}$. 2. XRD analysis shows that aging of the samples in the test does not change the structure of the sodium beat-alumina samples. 3. Examination in an SEM shows that grain size of the sodium beta-alumina is 1-3 microns.. 4. Ageing in molten sodium hydroxide changes the surface structure of the samples. The main mechanisms seem to be as follows: - First 108 days: Dissolution of material from surface of grains. Mass loss is slow, or $1-2 \times 10^{-3} \text{ %/day}$. - After 108 days: Dissolution of material from grain boundaries, leading to freeing of single grains from the surface. Mass loss is more rapid, or $8 \times 10^{-3} \text{ %/day}$. 5. In an electrolysis cell for production of sodium metal, by electrolysis of sodium hydroxide, it can be expected that the sodium beta-alumina membrane will lose about 7.3 % of its mass in 5 years or 14,7% in 10 years, assuming that long term corrosion rates are the same as measured in this project. 6. In an economic analysis of a process for production of sodium metal by electrolysis of sodium hydroxide in sodium beta-alumina electrolysis cells it was assumed that the cells would last for 2 years. The results obtained in this project indicate that corrosion of sodium beta-alumina will not be an obstruction when designing a cell with a minimum lifetime of 2 years.					

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Lifetime of Sodium β'' - Alumina Membranes in Molten Sodium Hydroxide

Final Report

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Summary

Sodium metal can be made by electrolysis of molten sodium hydroxide in sodium β'' -alumina membrane electrolysis cells. However, there are some uncertainties about the lifetime of the sodium β'' -alumina membranes in contact with molten sodium hydroxide. The main objective of this project is to address these uncertainties and to study if the properties of the membrane degrade upon long term contact with molten sodium hydroxide. Electrolysis cells were designed, but it proved impossible to test them because the potentiostat that was to be used was designed for low current density. It therefore turned out to be impossible to do electrolysis tests with this experimental set-up. Instead, samples of sodium β'' -alumina disk were aged in molten sodium hydroxide for up to 149 day. Mass loss was only 0,15 % in the first 108 days, but in the next 41 days mass loss accelerated considerably, or up to 0,33% in 41 days. No change in the phase composition of the material was observed in the 149 days. Investigation of aged samples with SEM (Scanning electron microscopy) revealed that the molten sodium hydroxide preferably dissolved material at grain boundaries, which most likely resulted in freeing of grains (1 – 3 μm diameter) from the bulk of the material.

1 Introduction

Sodium borohydride (SBH) is now widely used as a reducing agent in the chemical industry. SBH can also be used to produce hydrogen for fuel cells. For that application it has the advantage of generating humidified pure hydrogen ready for use in fuel cells. The US based company Millennium Cell (<http://www.millenniumcell.com/>) has invented and developed the so-called “Hydrogen in Demand Technology”, generating hydrogen from sodium borohydride. The most promising applications of this technology are in portable applications using fuel cell technology instead of battery, both for military and civil use. A significant market for sodium borohydride will therefore be generated with increased use of this technology. The single most important barrier to overcome is the price of sodium borohydride. Therefore low cost sodium borohydride from Iceland, where advantage is taken of relatively inexpensive electric energy and geothermal steam, may indeed support such a development. The results of a previous cooperation between IceTec, Icelandic New Energy and Millennium Cell showed that the cost of producing sodium borohydride in Iceland, using a specially developed production process, is highly competitive compared with the world market price of sodium borohydride (Gunnarsson 2004; Ingólfsson 2004). In this process, sodium metal is reacted with hydrogen to yield sodium hydride, which is then reacted with trimethoxyborane to yield SBH. The sodium hydroxide obtained is recycled and used to make sodium metal in sodium β'' -alumina membranes electrolysis cells. However, there are still some technical uncertainties regarding this specially developed process and further investigation and research is therefore needed. The largest challenge, and the single most technical uncertainty in this process, concerns the production of sodium metal from sodium hydroxide, using sodium β'' -alumina membranes electrolysis cells. The main uncertainty is about the lifetime of sodium β'' -alumina membranes in contact with the molten sodium hydroxide. The main objective of this project is to address this uncertainty and to study if long time contact of sodium β'' -alumina with molten sodium hydroxide at 330 - 350 °C will affect properties of sodium β'' -alumina membranes, particularly the sodium ion conductivity of the sodium β'' -alumina.

In this progress report we describe work which took place in the period April 2007 to June 2008.

This project is supported by USAF European Office of Aerospace Research and Development, under award No. FA8655-07-1-3064.

2 Methods, Assumptions and Procedures

In this section, the experimental procedures used in the project are described.

2.1 Design and construction of electrolysis cells

Sodium β'' -alumina membranes were purchased from Ionotec ltd. (www.ionotec.com). These were small membranes disks (20 mm in diameter and 2 mm thick) and tubes (length = 70 mm, internal diameter 6.5 mm, wall thickness 1.5 mm). All parts coming into contact with the molten sodium hydroxide should preferably be made of pure nickel. Therefore, nickel beakers, closed end tubes for thermocouples tubes, wires etc., were ordered. Assemblies of the cathode and sodium β'' -alumina tubes were designed and made, see Figure 1.



Figure 1. Assemblies of nickel anodes and sodium β'' -alumina tubes in the course of preparation. The sodium-alumina tubes are 70mm long.

Equipment for electrochemical measurements was set up and initial measurement made on some test specimens. Electrochemical measurements were to be carried out with a Gamry Instruments PC4/300 potentiostat for electrochemical impedance spectroscopy. The maximum current for that instrument is 300 mA. In the first experiments carried out with the assemblies shown in Figure 1 it became clear that as the test developed, the measured current always exceeded the maximum of 300 mA. It was therefore impossible to obtain meaningful data with this experimental set-up. The tests were thus abandoned.

2.2 Ageing of membranes in molten sodium hydroxide

Disk made of sodium β'' -alumina (diameter 20 mm, thickness 2 mm) were used for ageing tests (delivered by Ionotec Ltd). The disks were kept in an oven at 105 °C overnight, then removed from the oven and cooled in nitrogen atmosphere. The mass of the disks was then measured. Nine disks were suspended in nickel wires and placed in molten sodium hydroxide at 340°C. Three disks were then removed from the molten sodium hydroxide after 38 day, three more after 108 day and the last three after 149 days. The disks were washed with distilled water after removal from the molten sodium hydroxide until the pH of the wash

water was down to 8-9. Then the disks were dried in an oven at 105 °C overnight and cooled in nitrogen atmosphere. The mass of the disks was then measured.

Disks, both aged and as received were studied with scanning electron microscopy (SEM) and as well as with X-ray diffraction (XRD).

3 Results and Discussion

The mass loss of the disks after ageing for up to 149 days is shown in Table 1.

Table 1. Mass loss of sodium β'' -alumina disks after ageing in molten sodium hydroxide at 340°C for different times. Standard deviation is given in parenthesis.

Ageing time of disks (days)	Cumulative Mass loss (%)	Mass loss per day (%/day)
0 – 38	0,072 (0,005)	$1,89 \cdot 10^{-3}$
38 – 108	0,15 (0,01)	$1,11 \cdot 10^{-3}$
108 – 149	0,48 (0,05)	$8,05 \cdot 10^{-3}$

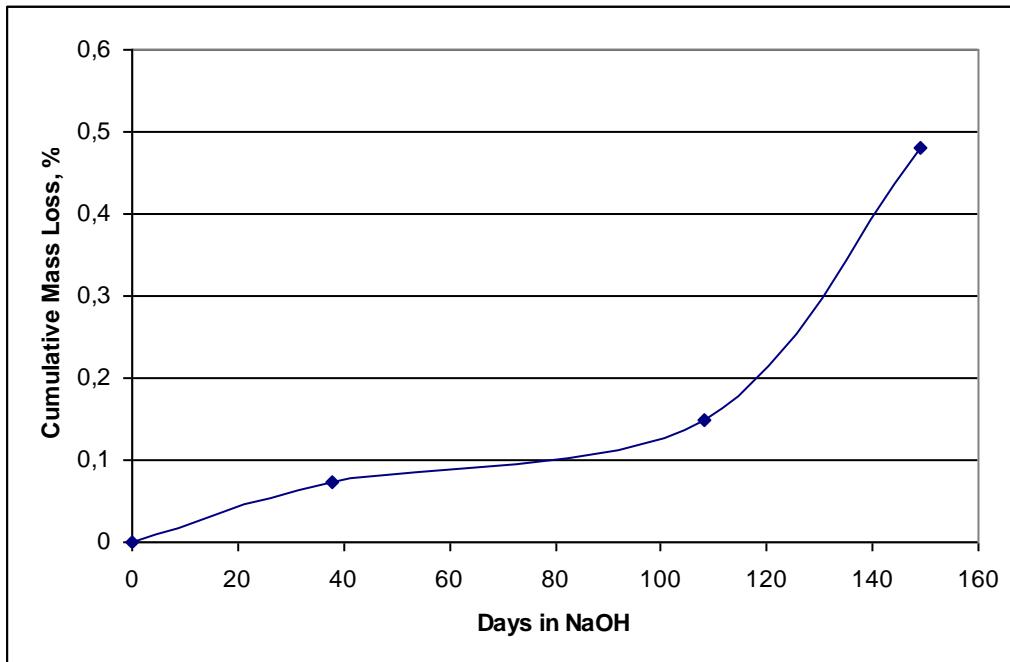


Figure 2. Cumulative mass loss of specimens in NaOH at 340°C.

Figure 2 shows the cumulative mass loss as a function of days in NaOH at 340°C. A significant acceleration of mass loss is seen after 108 days. Figure 3 shows the mass loss per day for the three periods, 1-38, 38-108 and 108-149 days. It is clear that mass loss accelerates considerably in the third period, after 108 days.

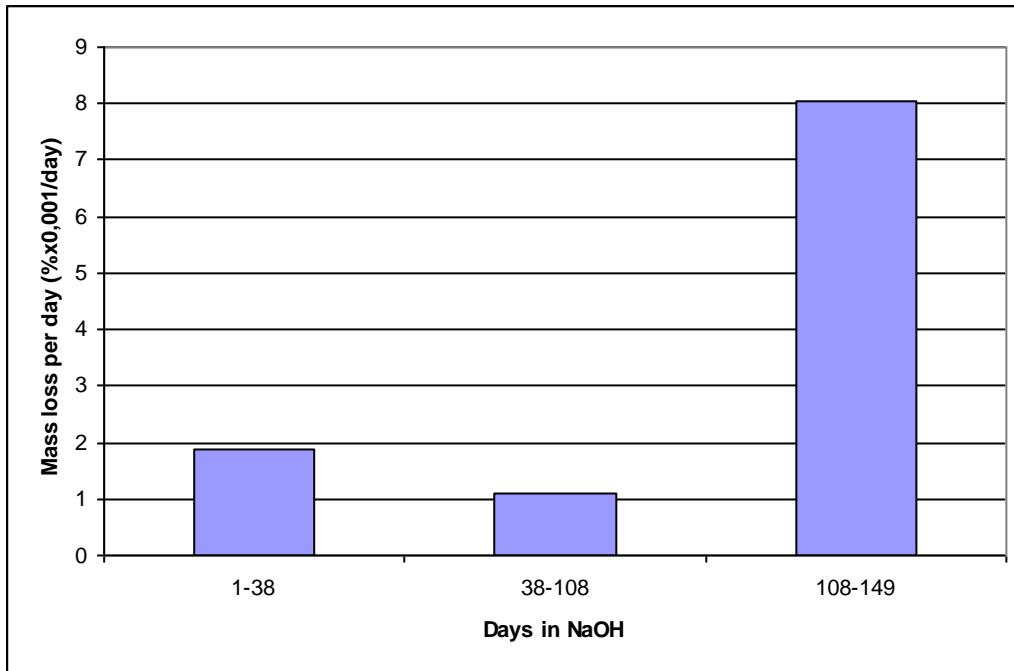
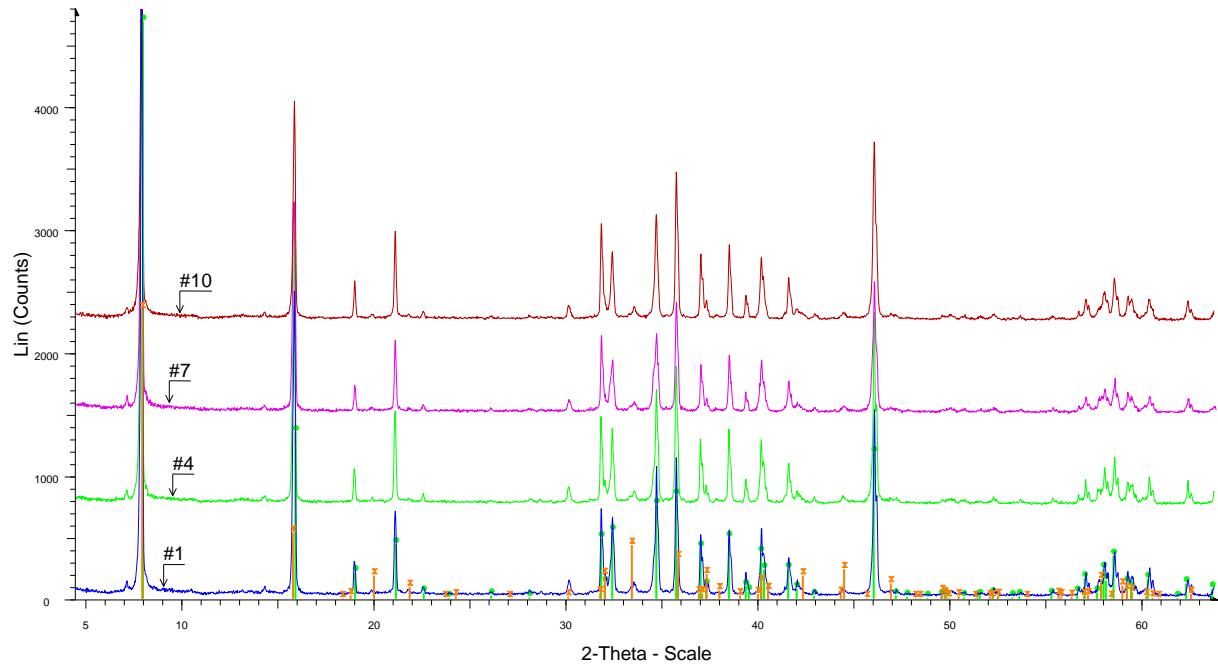


Figure 3. Mass loss per day for the three periods between measurements of mass of the specimens.

XRD analysis was done on the material before, during and after the aging tests. The results are shown in Figure 4.

43715/8HK07118 #1



█ 43715/8HK07118 #1 - File: 43715.raw - Type: 2Th/Th locked - Start: 3.771 ° - End: 63.806 ° - Step: 0.020 ° - Step time: 1. s - Time Started: 18 s - 2-Theta: 3.771 ° - Anode: Cu - WL1: 1.5406 - Generator kV: 40 kV - G
█ 43717/8HK07118 #4 - File: 43717.raw - Type: 2Th/Th locked - Start: 3.771 ° - End: 63.806 ° - Step: 0.020 ° - Step time: 1. s - Time Started: 16 s - 2-Theta: 3.771 ° - Anode: Cu - WL1: 1.5406 - Generator kV: 40 kV - G
█ 43719/8HK07118 #7 - File: 43719.raw - Type: 2Th/Th locked - Start: 3.919 ° - End: 63.932 ° - Step: 0.020 ° - Step time: 1. s - Time Started: 15 s - 2-Theta: 3.919 ° - Anode: Cu - WL1: 1.5406 - Generator kV: 40 kV - G
█ 43721/8HK07118 #10 - File: 43721.raw - Type: 2Th/Th locked - Start: 3.756 ° - End: 63.793 ° - Step: 0.020 ° - Step time: 1. s - Time Started: 18 s - 2-Theta: 3.756 ° - Anode: Cu - WL1: 1.5406 - Generator kV: 40 kV - G
█ 01-084-0214 (N) - Alumina - Na1.67Mg0.67Al10.33O17 - Y: 76.04 % - d x by: 1. - WL: 1.5406 - Rhombo.Haxes - a 5.62300 - b 5.62300 - c 33.53600 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - R-3m (P-3m)
█ 01-079-1560 (N) - Diaoyudaoite, syn - Na1.22Al11O17.11 - Y: 38.14 % - d x by: 1. - WL: 1.5406 - Hexagonal - a 5.59290 - b 5.59290 - c 22.52600 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63/mmc (P-63/mmc)

Figure 4. XRD spectra of sodium β'' -alumina (labelled Alumina – $\text{Na}1.67\text{Mg}0.67\text{Al}10.33\text{O}17$) disks after ageing in molten sodium hydroxide at 340°C for different times. #10 is as received sample sample, #1, #4 and #7 are aged 38, 108 and 149 days respectively.

The XRD analysis shows that the disks are mainly made of sodium β'' -alumina, and that they contain a small percentage of sodium β -alumina (diaoyudaoite) as is often found in sodium β'' -alumina (Stevens 1991). The results of the XRD analysis show that aging of the samples in the test does not change the structure of the sodium β'' -alumina samples.

Samples were also investigated with a Scanning Electron Microscope. A selection of images is shown in Figures 5 to 8.

In the as received sample, see Figure 5, some small grains are visible on the surface as well as some porosity. In the micrograph at higher magnification (Figure 3b) it is possible to see some grain boundaries. In sodium β'' -alumina, porosity is most often found at grain corners and the grain size is often 1 – 2 μm (Stevens 1991).

After ageing for 38 days in molten sodium hydroxide the structure of the surface changed considerably, see Figure 6. It seems that some material in between small grains, that are only fraction of a μm , has been etched away. Some larger grains, 1 – 3 μm in diameter, are also seen. The small grains seem to be a part of the larger grains. It is also noteworthy that grain boundaries between the 1- 3 μm grains can now be more clearly seen than in the as received sample, the molten sodium hydroxide seems to preferentially dissolve material at grain boundaries.

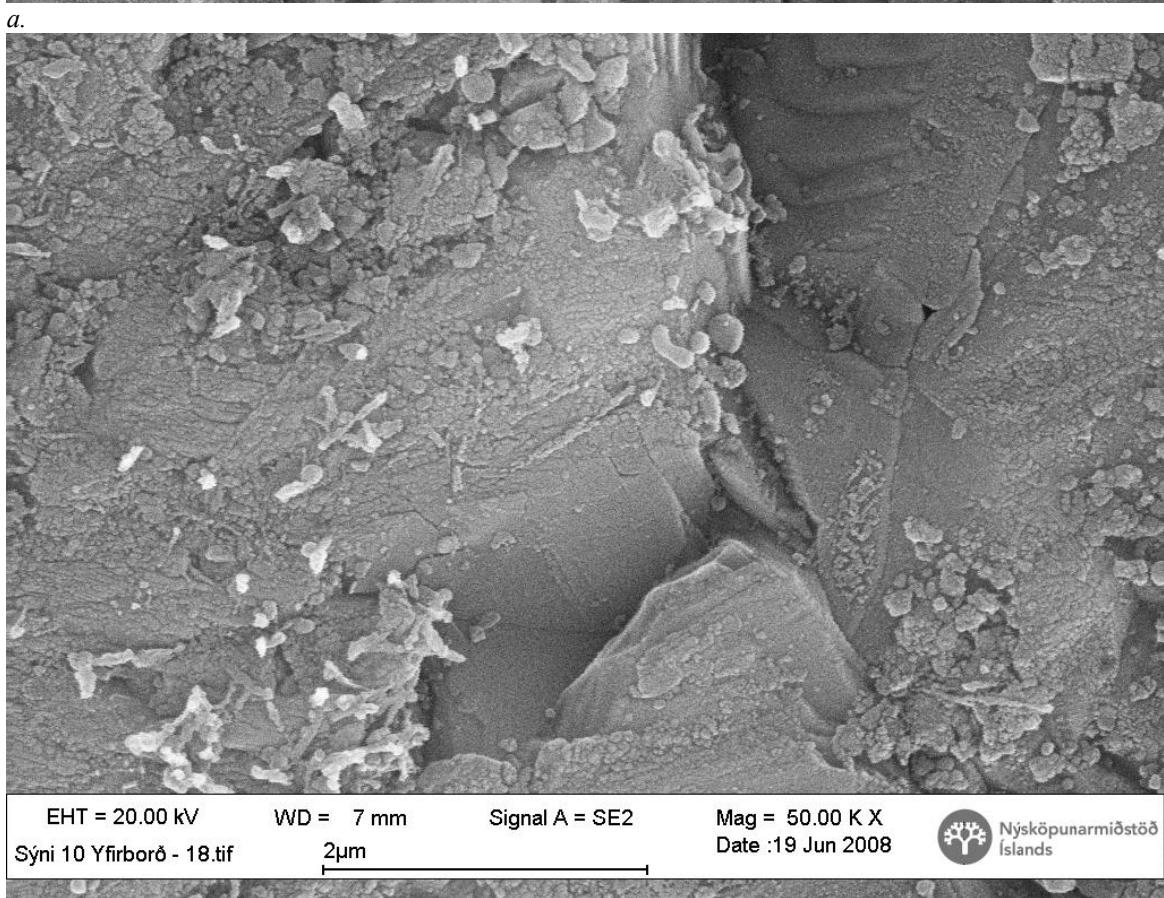
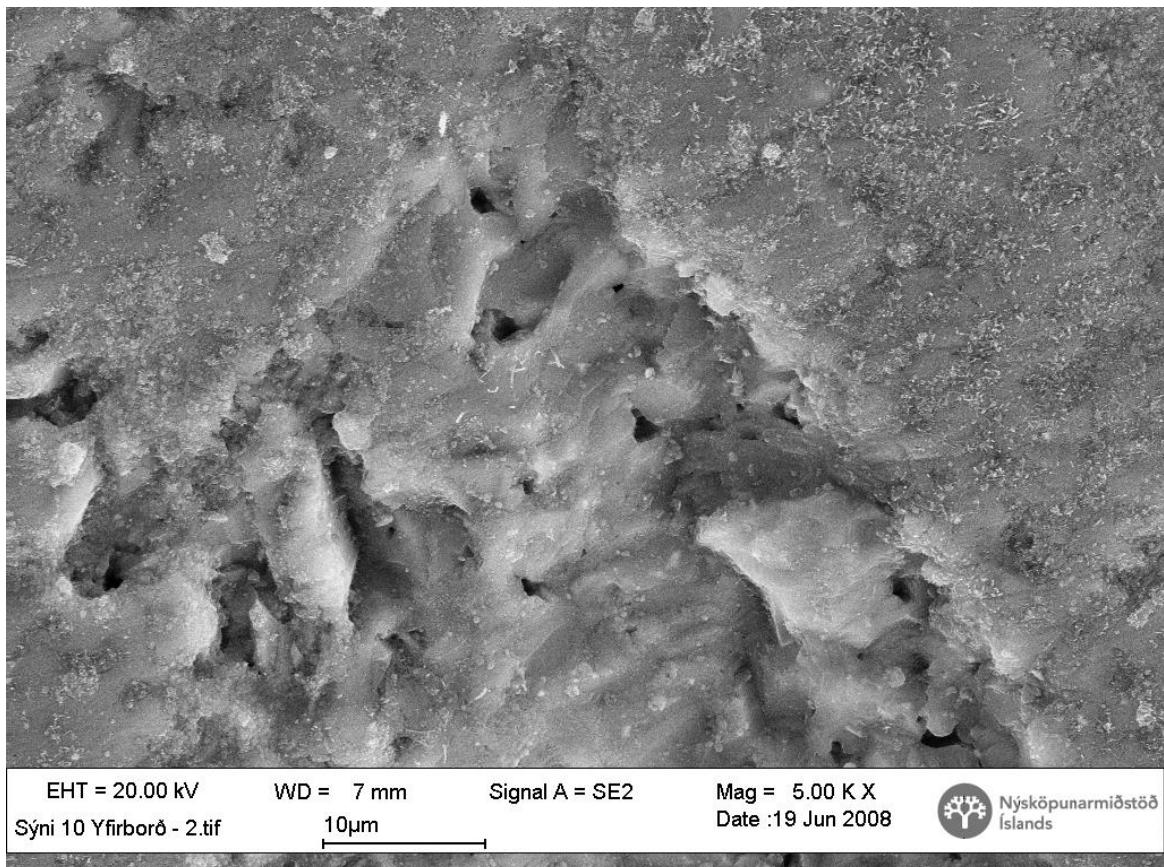
The dissolution of material from grain boundaries is more clearly seen in samples aged for 108 days, see Figure 7, and especially for 149 days, see Figure 8. In the samples aged for 149 days it is clearly seen that the sodium β'' -alumina disks received are made of material with about 1 – 3 μm grain size.

The thickness of the disks is 2 mm. A mass loss of 0,1% corresponds to a thinning of the disks by 2 μm or 1 μm on either side of the disks, assuming that the mass loss is evenly distributed over the surface of the disks and that the effect of the edges is neglected. The mass loss in the period between 108 and 149 days is 0,33% corresponding to a thinning of the disk by 6,6 μm or 3,3 μm on either side. Therefore in the period between 108 and 149 days the disks have lost about 1- 2 layers of sodium β'' -alumina grains from the surface of the disks.

Based on the above observation, the corrosion of the sodium β'' -alumina in molten sodium hydroxide seems to proceed according to the following processes

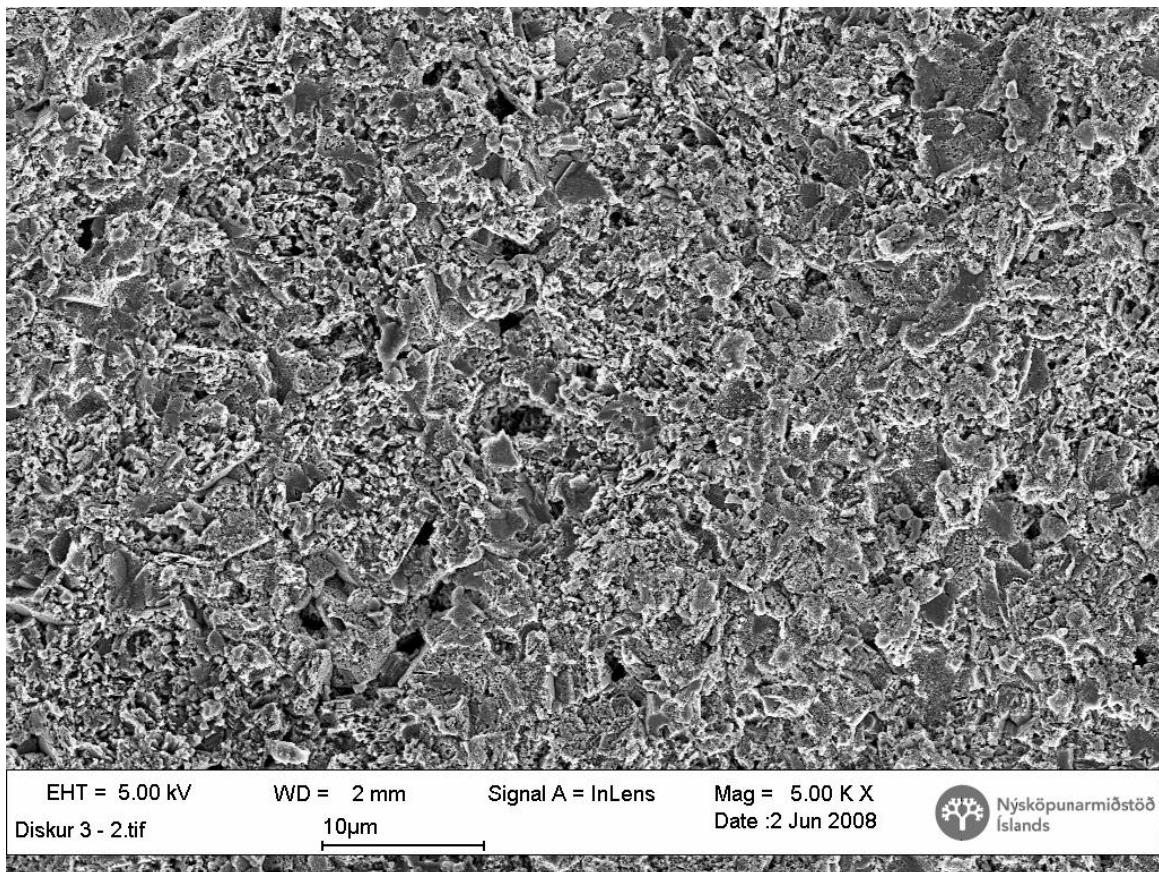
- Material is dissolved from the surface of the 1 – 3 μm grains. The mass loss associated with this process is relatively small and it can be estimated to be of the order seen in the first 108 days.
- Material is dissolved from grain boundaries, eventually resulting in “freeing” of single grains from the surface. This process seems to speed up the corrosion of the sodium β'' -alumina.

When trying to estimate the lifetime of the sodium β'' -alumina membranes, in the light of these results, it seems appropriate to assume that the corrosion rate is at least as high as in the period between 108 and 149 days ($8,05 \cdot 10^{-3}$ % per day), and that the period up to about 109 days could be regarded as an incubation time.

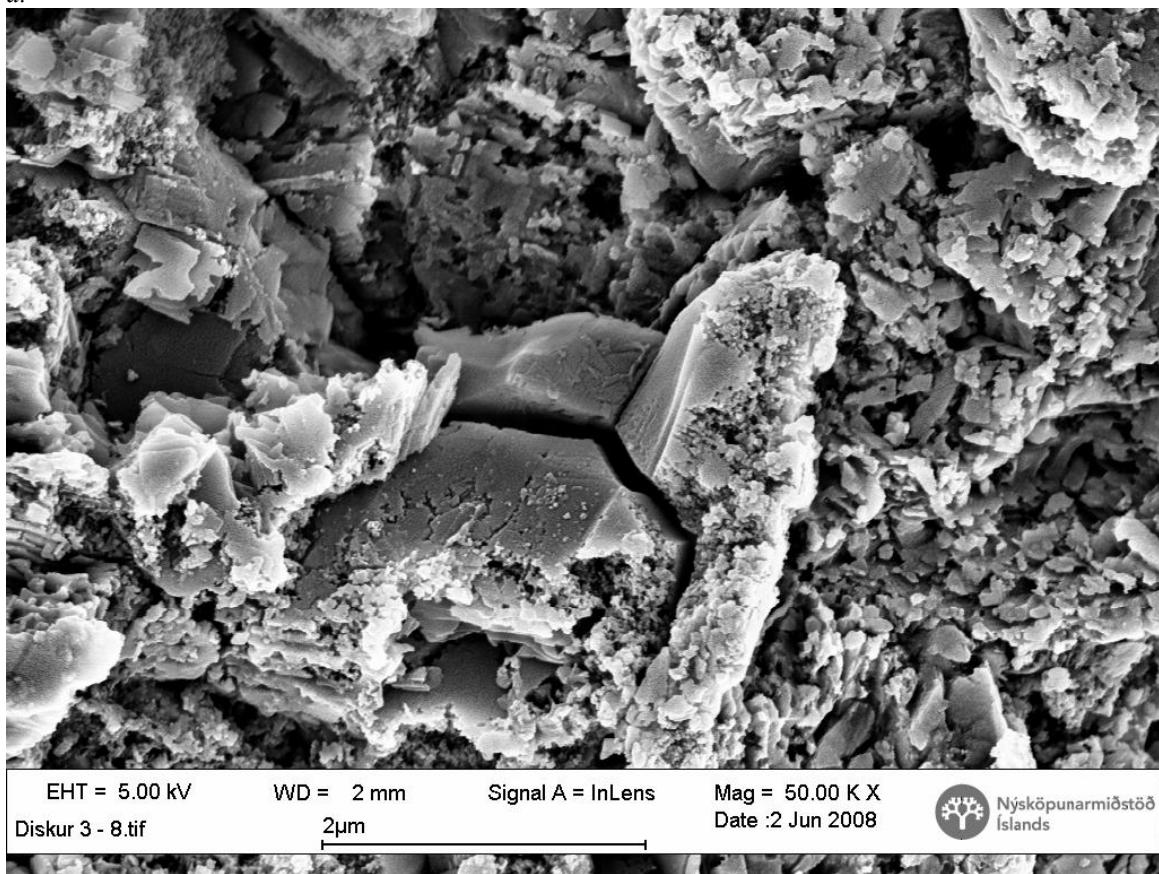


b.

Figure 5. Scanning electron micrographs of as received sample at a) 5.000x and b) 50.000x magnification.

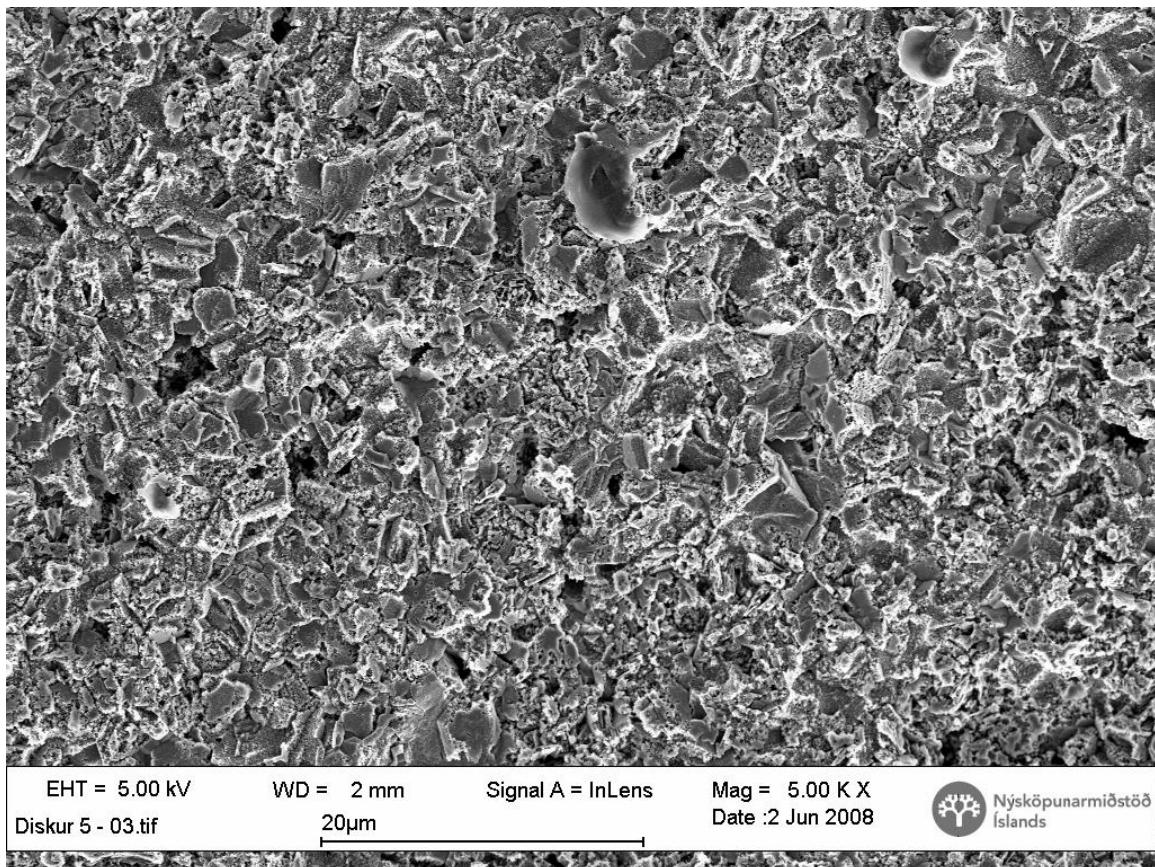


a.

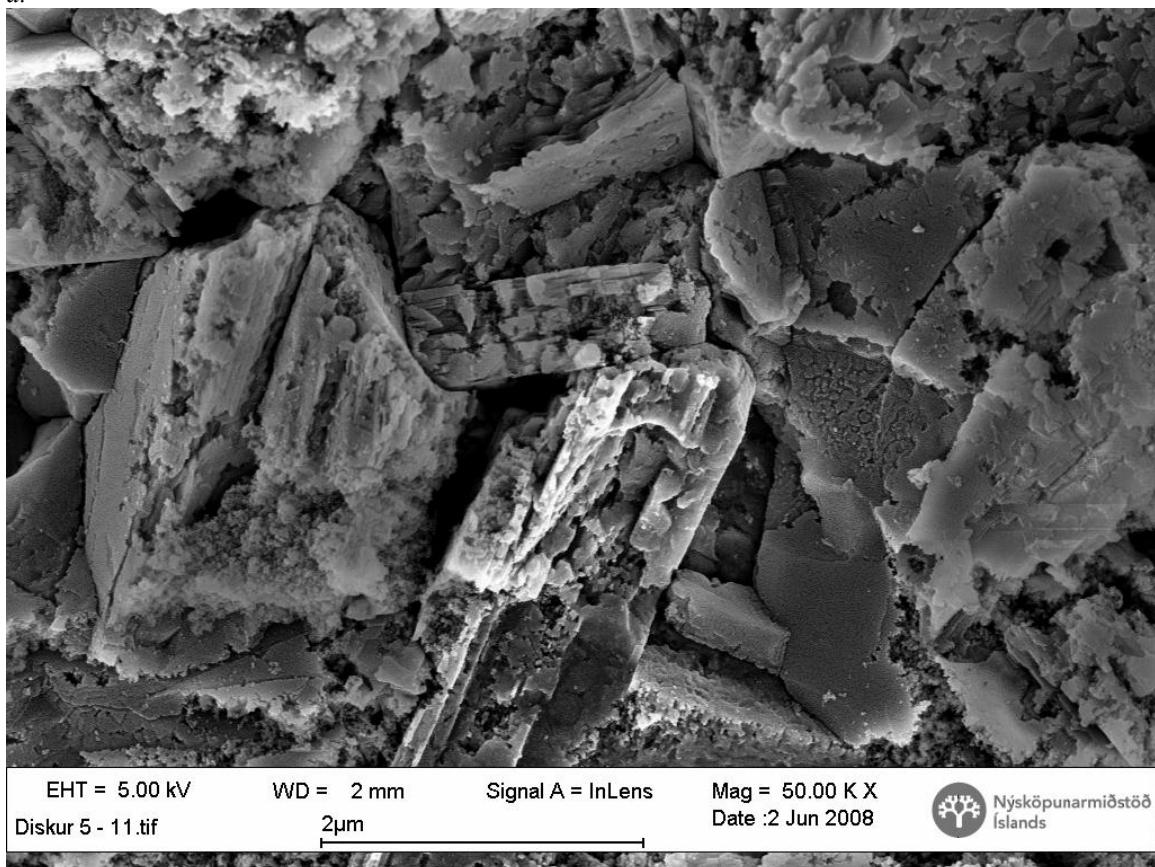


b.

Figure 6. Scanning electron micrographs of sample aged 38 days at a) 5.000x and b) 50.000x magnification.

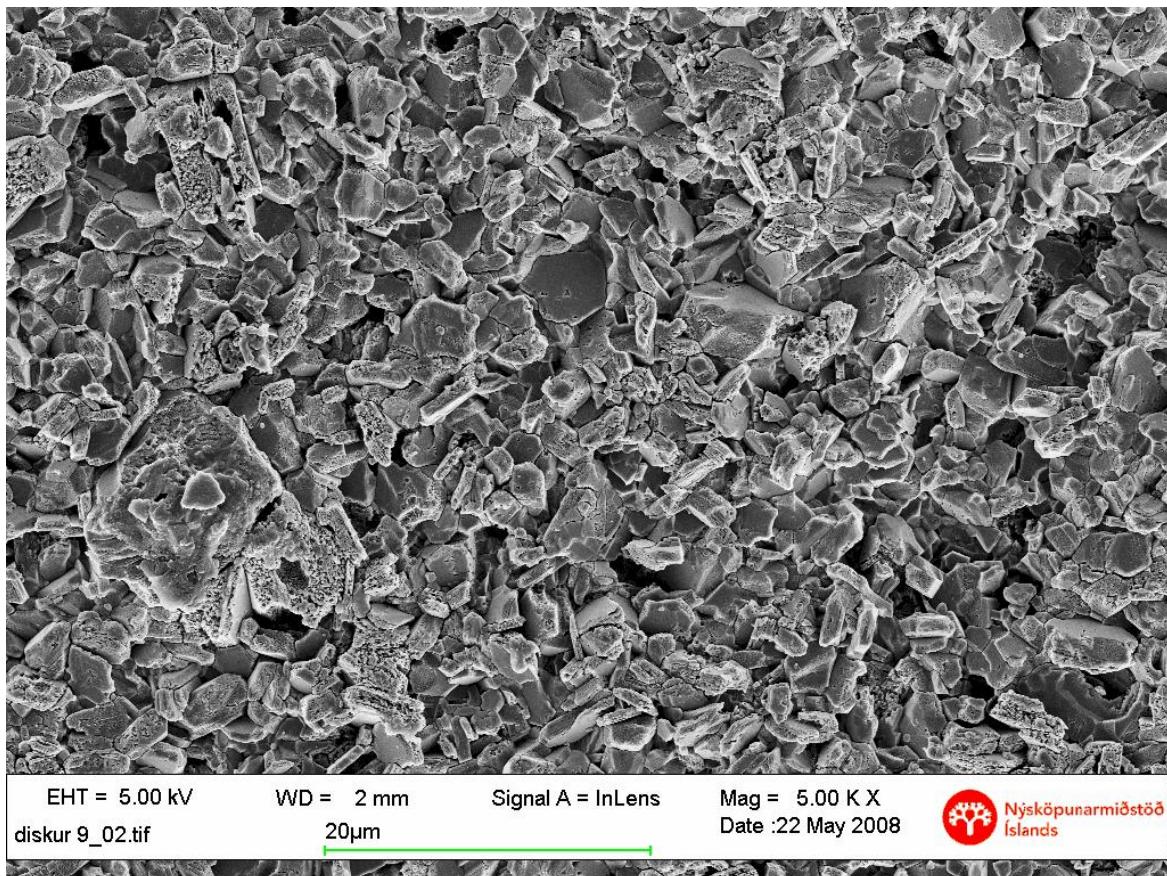


a.

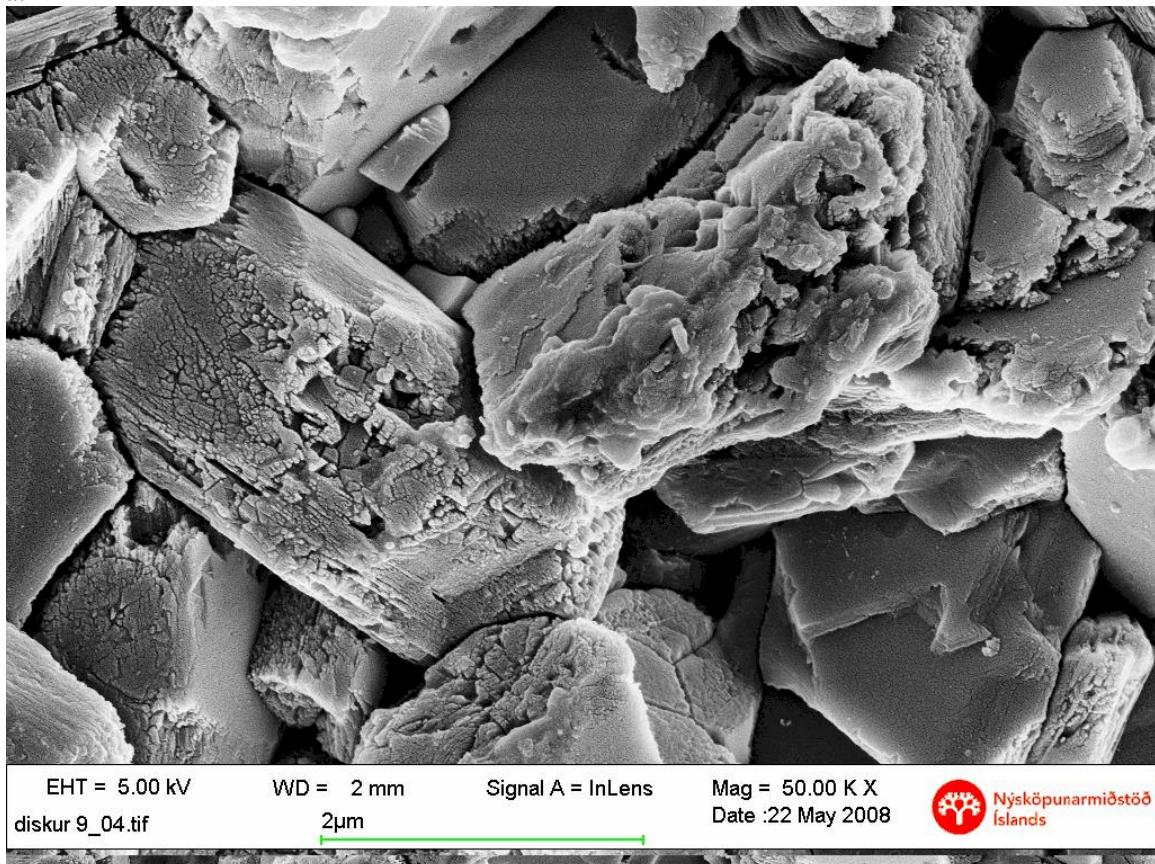


b.

Figure 7. Scanning electron micrographs of sample aged 108 days at a) 5.000x and b) 50.000x magnification.



a.



b.

Figure 8. Scanning electron micrographs of sample aged 149 days at a) 5.000x and b) 50.000x magnification.

In an electrolysis cell for production of sodium metal by electrolysis of sodium hydroxide, the sodium β'' -alumina is in contact with molten sodium hydroxide on one side of the membrane and with molten sodium on the other side of the membrane. If it is assumed that the membrane does not corrode on the sodium metal side, and that the long term corrosion rates are the same as measured in the last 41 days. The results obtained here show that the sodium β'' -alumina membrane will lose 7,3 % of its mass in 5 years and 14,7 % of its mass in 10 years. Although the mass loss could be considerably higher, the actual lifetime is expected to be considerably longer than assumed in the economic evaluation of the process (Ingólfsson 2004). Here it was found that the cost of sodium metal could be lower than 1 \$/kg for a current density of $0,2 \text{ A/cm}^2$ if the lifetime of the cells was longer than 2 years (Ingólfsson 2004). The results obtained in this project indicate that corrosion of sodium β'' -alumina will not be an obstruction when designing a cell with a minimum lifetime of 2 years.

4 Conclusions

1. Sodium β'' -alumina membranes were aged in molten NaOH at 340°C for 38, 108 and 149 days respectively. Samples were weighed and investigated in an SEM after each period. Rate of mass loss increases significantly in the period after 108 days, or from $1\text{-}2\cdot10^{-3}\text{ %/day}$ to $8\cdot10^{-3}\text{ %/day}$.
2. XRD analysis shows that aging of the samples in the test does not change the structure of the sodium β'' -alumina samples.
3. Examination in an SEM shows that grain size of the sodium β'' -alumina is 1-3 μm .
4. Ageing in molten sodium hydroxide changes the surface structure of the samples. The main mechanisms seem to be as follows:
 - First 108 days: Dissolution of material from surface of grains. Mass loss is slow, or $1\text{-}2\cdot10^{-3}\text{ %/day}$.
 - After 108 days: Dissolution of material from grain boundaries, leading to freeing of single grains from the surface. Mass loss is more rapid, or $8\cdot10^{-3}\text{ %/day}$.
5. In an electrolysis cell for production of sodium metal, by electrolysis of sodium hydroxide, it can be expected that the sodium β'' -alumina membrane will lose about 7.3 % of its mass in 5 years or 14,7% in 10 years, assuming that long term corrosion rates are the same as measured in this project.
6. In an economic analysis of a process for production of sodium metal by electrolysis of sodium hydroxide in sodium β'' -alumina electrolysis cells it was assumed that the cells would last for 2 years. The results obtained in this project indicate that corrosion of sodium β'' -alumina will not be an obstruction when designing a cell with a minimum lifetime of 2 years.

5 References

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List of symbols, Abbreviations and Acronyms

XRD:	X-Ray Diffraction
SEM:	Scanning Electron Microscopy
SBH:	Sodium Borohydrate
US:	United States
USAF:	United States Air Force
NaOH:	Sodium Hydroxide
IceTec:	Technological Institute of Iceland, now Innovation center Iceland.